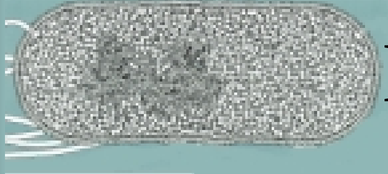


Maxwell, Collisions, and Diffusion

Class vote on Exam date

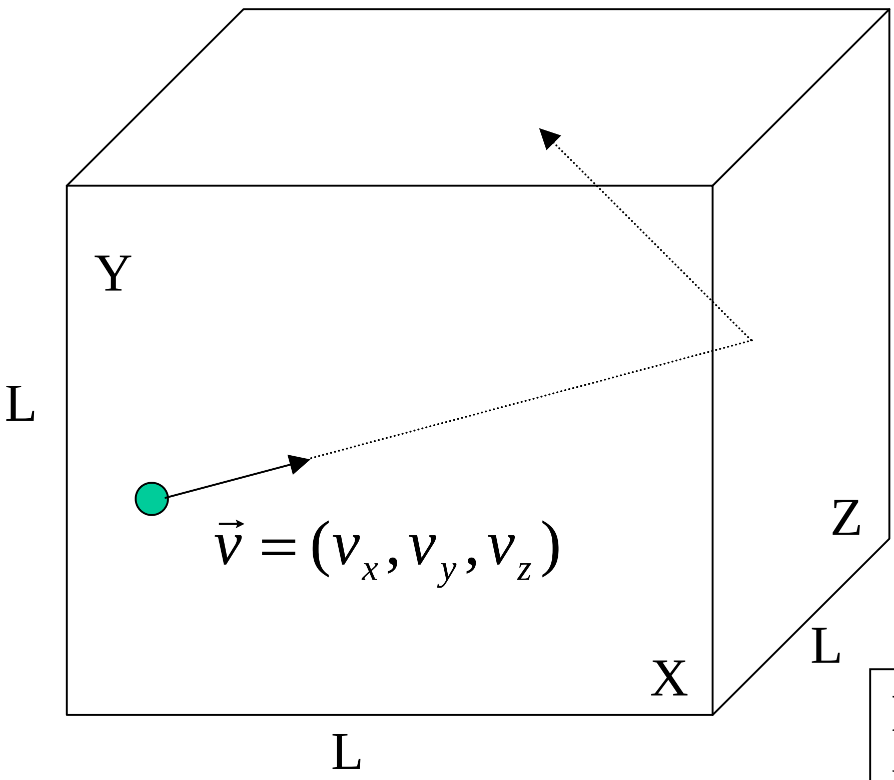
Topic for today's lecture:

Distributions of velocities (and energies)

Molecular Collision and Mean Free Paths

Diffusion

Last time we were considering a gas bumping about inside a square box.

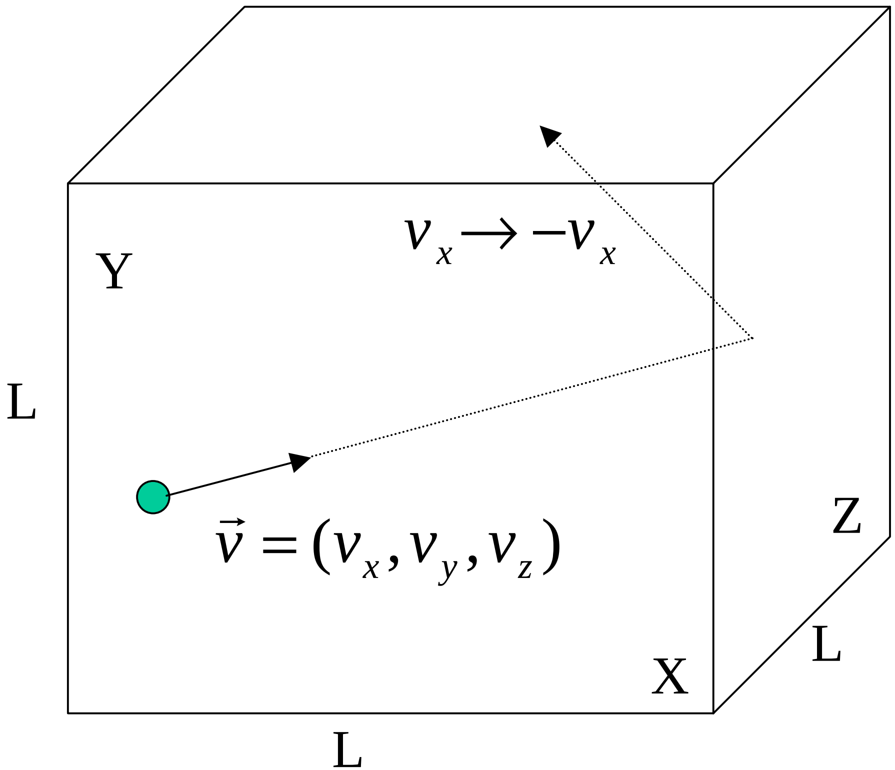


We assume:

1) Gases are composed of particles
2) Particles are in constant motion
3) Collision w/ walls --> Pressure
4) Collisions w/ walls are elastic
5) Large distances btw particles

6) Particles are point mass
7) No strong forces btw particles
   (Elastic collisions)

In a gas: the distance between particles is about 10 times the molecular diameter

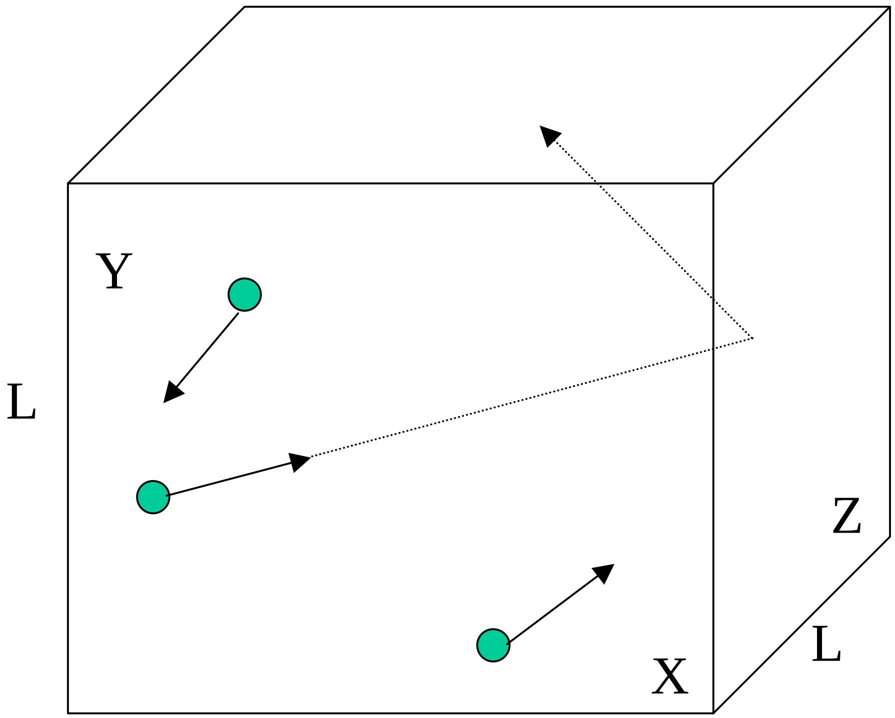


A set of simple assumptions led us to describe the change of momentum upon collisions with walls.

$$\Delta p = m * \Delta v_x = 2 * m * v_x$$

$$N_{collisions} / time = v_x / L$$

$$\boxed{\frac{dp}{dt} = 2 * m * v_x * v_x / L = 2 m v_x^2 / L}$$



This allowed us to related the pressure to the collisions of molecules with the walls.

$$\boxed{\left\langle \frac{dp}{dt} \right\rangle = 2m\langle v_x^2 \rangle / L = Force}$$

So pressure must be:

$$P = \frac{\left\langle \frac{dp}{dt} \right\rangle}{A} = \frac{2m\langle v_x^2 \rangle}{L * A} = \frac{2m\langle v_x^2 \rangle}{L * (2L^2)} = \frac{m\langle v_x^2 \rangle}{V}$$

Now we have to relate this to temperature. We can do so through kinetic energy.

$$\boxed{P_{tot} = \frac{Nm\left\langle v^2 \right\rangle}{3V}}$$

We know from basic physics that:

$$\left\langle U_{translation} \right\rangle = \frac{1}{2} m \left\langle v^2 \right\rangle = \frac{3}{2} kT$$

So now we have a connection between some microscopic data and macroscopic thermodynamic data. But ultimately we are also interested in rates of reaction.

For this we will need to consider:

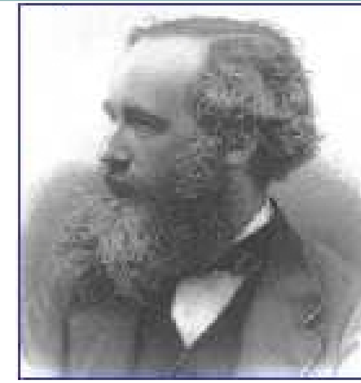
1) How frequently to molecules encounter each other?
2) How are they distributed in space?
3) Given an encounter how likely is it that a reaction will occur.

All of these depend in part on the distribution of velocities in a mixture of molecules.

We not been considering the fact that not every molecular has the same speed.

Boltzmann and Maxwell both derived statistical distributions for the fraction of particles having a particular velocity.

More generally, they derived distributions for the fraction of particles having a particular energy.



We will follow Maxwell’s procedure.

We ask what is the probability of finding a particle with a speed between

$$c \qquad \text{and} \qquad c+dC$$

We will consider only one direction (x) since all directions must be equivalent.

We denote the components of velocity in x,y,z by u,v,w!

The number of particles have a velocity between u and u+*d*u as

$$\boldsymbol{d\mathrm{n}_u}$$

Thus the probability of finding a particle within this velocity range is:

$$\boldsymbol{d\mathrm{n}_u/\mathrm{N}}$$

Now we make the following **assumptions**:

1) If *d*u is small enough, then doubling *d*u doubles $d\mathrm{n}_u$.

2) dn_u depends only on u, the velocity in the x direction.

3) Obviously, this number should not depend on the sign of u.

So we hypothesize a functional form for the equation;

$$\frac{dn_u}{N} = f(u^2)du$$

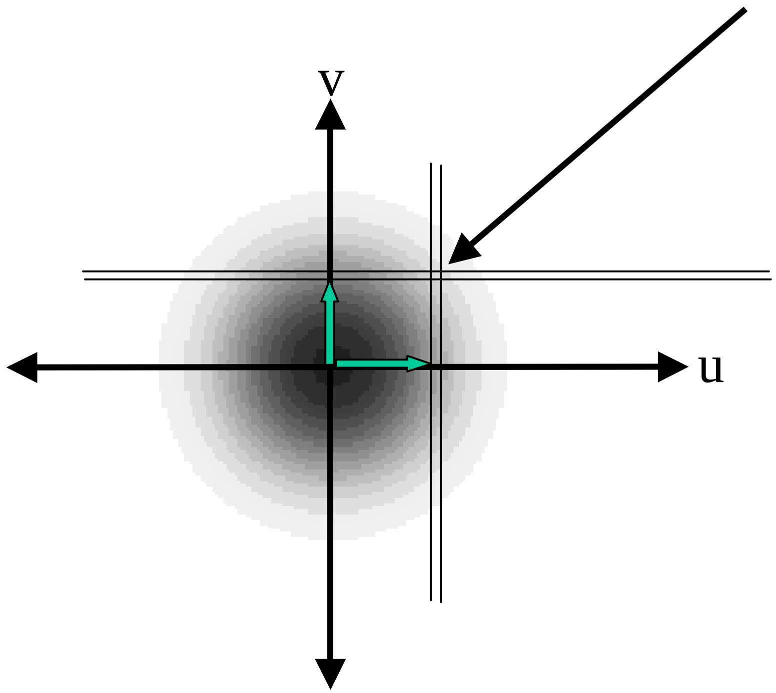
Why not |u| instead of u^2?

Remember now-- the equations for n_v and n_w will have exactly the same form if we neglect things like gravity or other external fields.

What is the fraction of molecules with x velocities between u and u+du and y velocities between v and v+ dv?

For independent probabilities this is very simple:

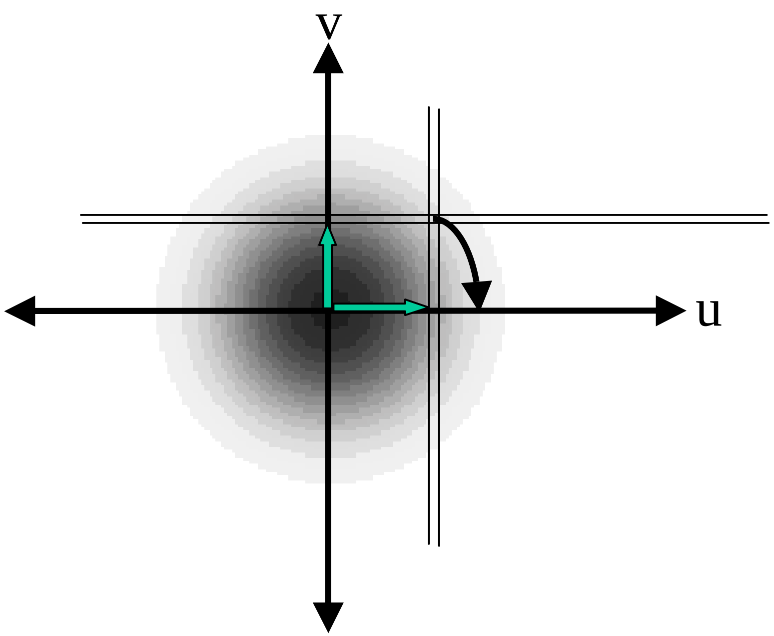
$$\frac{dn_{uv}}{N} = \left(\frac{dn_u}{N}\right)\left(\frac{dn_v}{N}\right) = f(u^2)\,f(v^2)\,du\,dv$$



We have simply multiplied the probabilities together.

The question now arises what are the *f*'s?

The answer comes by considering that the functions must be symmetric around the origin.



$$\boxed{\frac{dn_{uv}}{N} = \left(\frac{dn_u}{N}\right)\left(\frac{dn_v}{N}\right) = f(u^2)\,f(v^2)\,du\,dv}$$

That is the densities must be the same at these two points.

So

$f(u^2+v^2)*f(0)=f(u^2)*f(v^2)$

Since f(0) must be a constant we have:

$A* f(u^2+v^2) =f(u^2)*f(v^2)$

The only function that satisfies this is the exponential!

$$f(u^2) = Be^{-\beta u^2}$$

So for all three components:

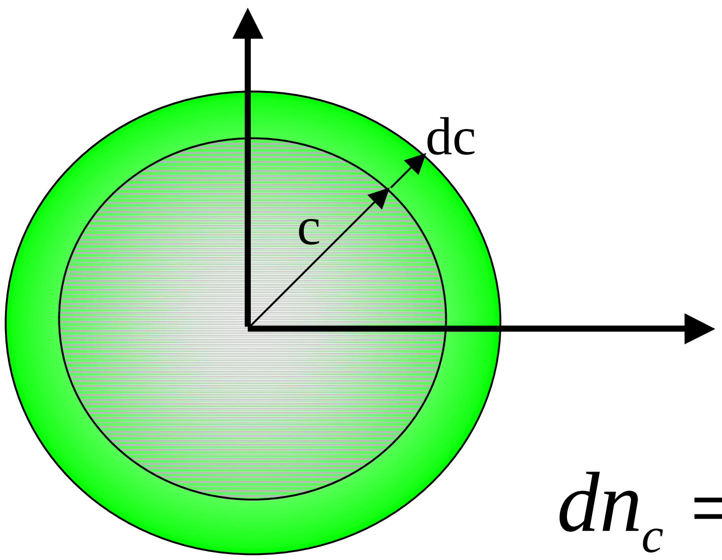
$$\frac{dn_{uv}w}{N} = \left(\frac{dn_u}{N}\right)\left(\frac{dn_v}{N}\right)\left(\frac{dn_v}{N}\right) = f(u^2)\,f(v^2)\,f(v^2)\,dudvdw$$
$$= B^3 e^{-\beta(u^2+v^2+w^2)}dudvdw$$

Note that if we want the point density at a particular speed then:

$$\frac{dn_{uvw}}{dudvdw} = NB^3 e^{-\beta(u^2+v^2+w^2)} = NB^3 e^{-\beta c^2}$$

$$\frac{dn_{uvw}}{dudvdw} = NB^3 e^{-\beta(u^2+v^2+w^2)} = NB^3 e^{-\beta c^2} = \rho_c$$

So if we want the number of particles with a speed between c and c + dc we take this point density and multiply it by the volume of the velocity space containing the speed range.



$$V_{shell} = \frac{4\pi}{3}(c+dc)^3 - \frac{4\pi}{3}(c)^3$$

$$= \frac{4\pi}{3}(3c^2dc + 3cdc^2 + dc^3)$$

$$\cong 4\pi c^2 dc$$

So,

$$dn_c = \rho_c * V_{shell} = 4\pi NB^3 c^2 e^{-\beta c^2} dc$$

$$dn_c = \rho_c * V_{shell} = 4\pi N B^3 c^2 e^{-\beta c^2} dc$$

So now we have a basic functional form for the number of molecules have a particular velocity!

All we have to do is find B and β.

We do this using normalization conditions.

We know that:

1) $$N = \int_{c=0}^{c=\infty} dn_c$$

and that the average kinetic energy is:

2) $$< u >= \frac{\int_{c=0}^{c=\infty} \frac{1}{2} mc^2 dn_c}{N}$$

From the first of these we get: $B^3 = \left(\frac{\beta}{\pi} \right)^{3/2}$

Using

$$dn_c = \rho_c * V_{shell} = 4\pi N B^3 c^2 e^{-\beta c^2} dc$$

We get

$$< u > = \frac{\int_{c=0}^{c=\infty} \frac{1}{2} m c^2 dn_c}{N} = 2\pi m \left(\frac{\beta}{\pi} \right)^{3/2} \int_{c=0}^{c=\infty} c^4 e^{-\beta c^2} dn_c$$

Given that <u> is also 3/2 kT and looking up the integral in a table gives:

$$\beta = \frac{m}{2kT}$$

AND

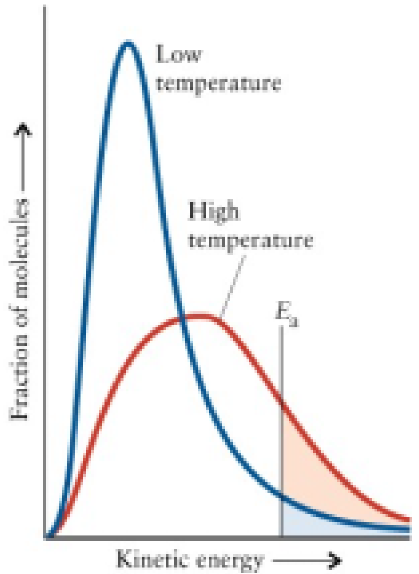
$$B = \left(\frac{m}{2\pi kT} \right)^{1/2}$$

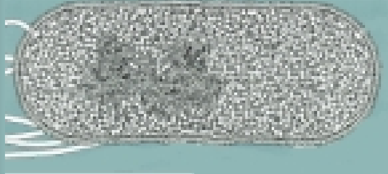
Plugging these values back into our original equation for dn_c

$$dn_c = 4\pi NB^3 c^2 e^{-\beta c^2} dc$$

We get:

$$\frac{1}{N}\frac{dn_c}{dc} = 4\pi\left(\frac{m}{2\pi kT}\right)^{3/2} c^2 e^{-\frac{mc^2}{2kT}}$$





To calculate the average speed of a molecule:

$$< c >= \int_0^\infty c \frac{1}{N} \frac{dn_c}{dc} dc = \int_0^\infty cP(c)dc$$

Using equations like this is it straightforward to derive:

$$< c >= \sqrt{\frac{8kT}{\pi m}} = \sqrt{\frac{8RT}{\pi M}}$$

$$< c^2 >= \frac{3kT}{m}$$

We can now begin to derive some transport properties.

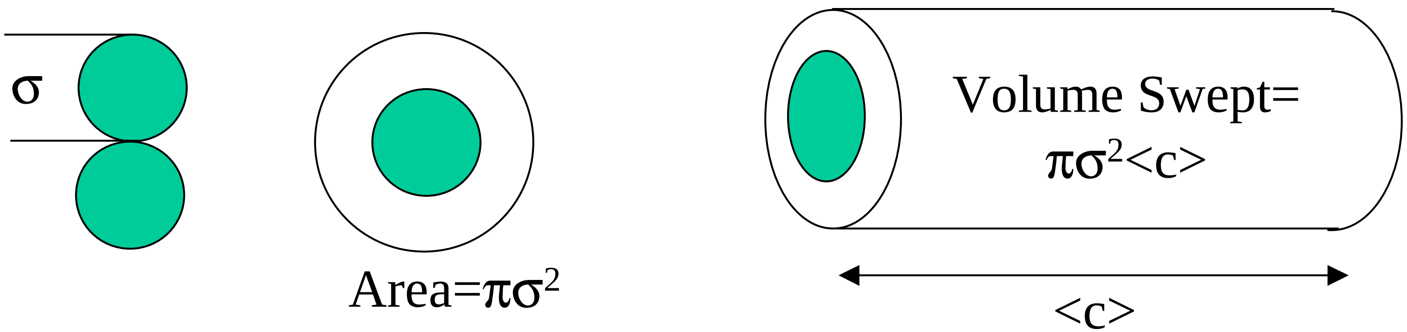
For example the mean free path can be calculated:

$\boxed{\lambda\text{= mean free path= average distance between collisions}}$

In one second a molecule travels $\langle c\rangle$*1s meters and makes Z_1 collisions. Thus:

$$\lambda = \langle c\rangle / Z_1$$

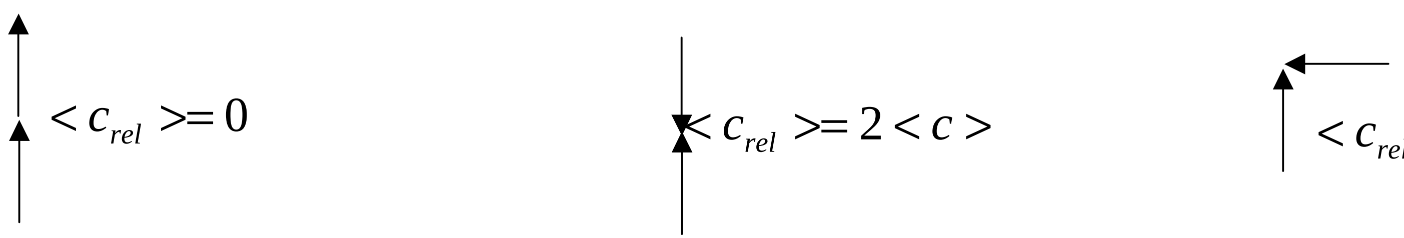
We calculate Z_1 using the following picture



The number of molecules encountered within that volume is:

$$N_1 = \pi\sigma^2<c>*N/V$$

Now the number of collision has comes out of this by realizing that it is the relative velocities that matter!



$$<c_{rel}> = 0 \qquad <c_{rel}> = 2<c> \qquad <c_{rel}> = \sqrt{2}<c>$$

$$Z_1 = (0.5)^{1/2}\pi\sigma^2<c_{rel}>*N/V$$

$\lambda = \langle c \rangle / Z_1$

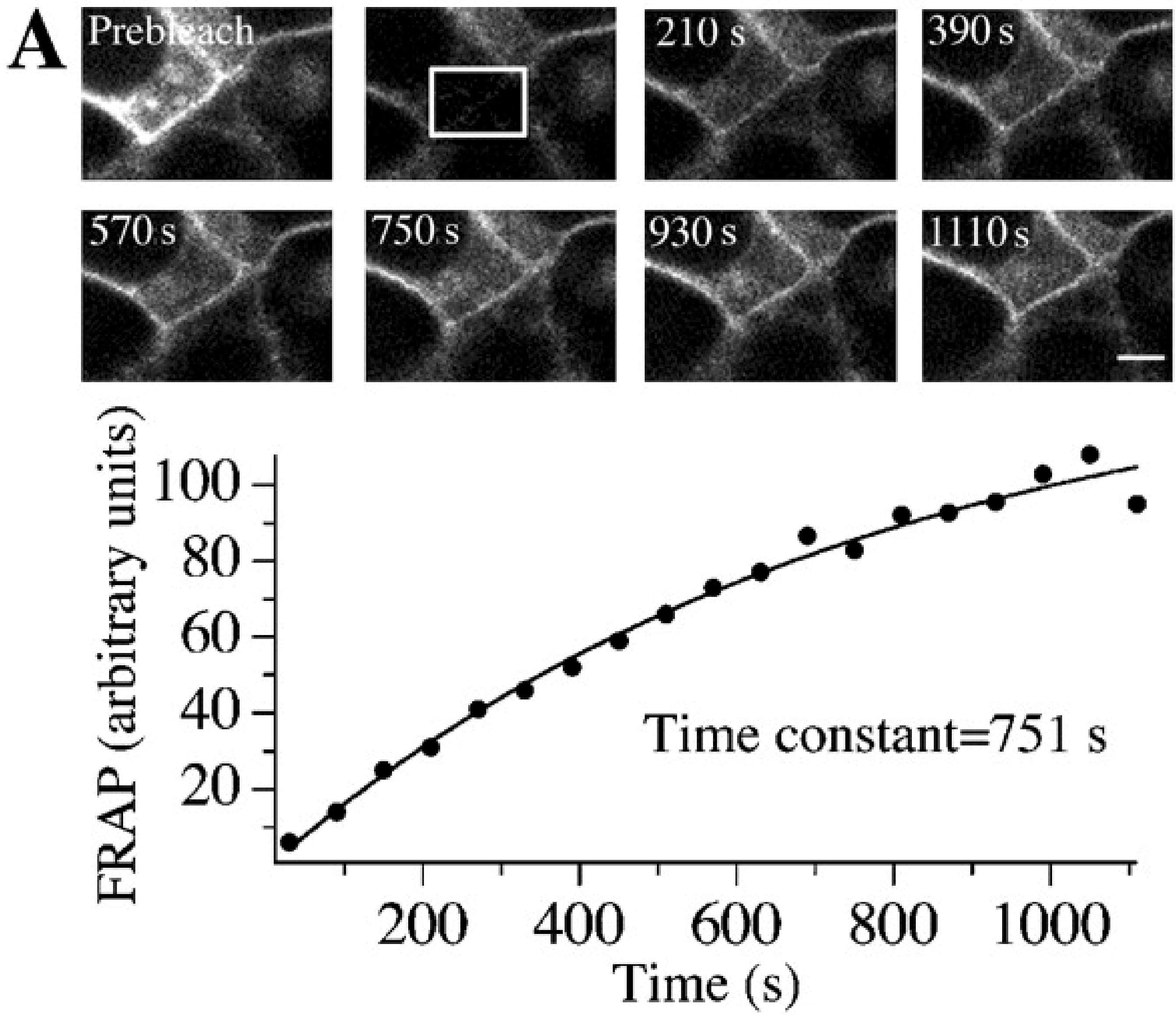
$Z_1 = (0.5)^{1/2}\pi\sigma^2 \langle c_{rel} \rangle * N/V$

$$\lambda = \frac{1}{\sqrt{2}\pi\sigma^2 \frac{N}{V}}$$

Thus the mean free path is dependent on molecular radius and the density of the gas.

At each collision the particle will be deflected off in another direction.

How long does it take a particle to move a given distance from a starting point?


A
Prebleach
210 s
390 s
570 s
750 s
930 s
1110 s
FRAP (arbitrary units)
100
80
60
40
20
200
400
600
800
1000
Time (s)
Time constant=751 s